



Au decorated Pd nanowires for methane oxidation to liquid C1 products

Yueshan Xu¹, Daoxiong Wu¹, Peilin Deng^{*}, Jing Li, Junming Luo, Qi Chen, Wei Huang, Chong Michael Shim, Chunman Jia, Zhongxin Liu, Yijun Shen, Xinlong Tian^{*}

State Key Laboratory of Marine Resource Utilization in South China Sea, Hainan Provincial Key Lab of Fine Chemistry, School of Chemical Engineering and Technology, Hainan University, Haikou 570228, China

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ABSTRACT

The direct methane (CH₄) oxidation to high value-added C1 chemicals is a great promising strategy to explore the CH₄ resource utilization. However, the low activity and selectivity of catalytic performance remains a great conundrum due to the difficulty to activate the C—H bond and the unmanageable over oxidation. Herein, Pd_xAu_y nanowires (NWs) with various Pd/Au atomic ratios are presented as ideal models to explore the atomic-level effect of PdAu atoms for the direct CH₄ oxidation. The influence of reaction parameters are systematically investigated, and Pd₉Au₁ NWs display a maximum yield of 2890.3 μmol g⁻¹ h⁻¹ with 99% selectivity for the liquid C1 oxygenated products. This enhanced performance is attributed to the combination of one-dimensional structure and the synergistic effect from the suitable portion of Au on Pd sites, which regulates bond strength between adsorbed radicals (•OH, •OOH, •CH₃) and PdAu atoms, confirmed by the density function theory calculations.

1. Introduction

CH₄ is a highly efficient and clean energy that widely distributed in the earth's crust and oceans. CH₄ oxidation to high added-value chemical feedstocks such as olefins, aromatics, and small molecule alcohols not only meet various chemical materials, but also realize the efficient CH₄ resource utilization.[1–3] Due to the extremely high bond energy (439.3 kJ·mol⁻¹) and weak polarity of the C—H bond in CH₄ molecule, the activation of C—H bond is very challenging.[4,5] In addition, the highly active intermediates from the CH₄ activation are prone to be over-oxidized or a complete oxidation to carbon dioxide (CO₂), which severely decrease the selectivity of target products.[6–9] Currently, CH₄ is firstly converted into syngas (H₂ and CO) by the water vapor reforming method, and afterwards CH₃OH is obtained by the Fischer-Tropsch synthesis through the indirect steps.[10–12] These processes are quite complicated and require harsh reaction conditions as well as energy-consuming.[13–16] Therefore, the direct CH₄ partial oxidation to C1 chemicals with high activity and selectivity is greatly desirable under relatively mild conditions.

Recently, bimetallic PdAu have emerged as a representative catalyst for the direct CH₄ oxidation under mild conditions with H₂O₂ as the oxidant.[17–20] Hutchings et al. reported a radical reaction mechanism

involving methyl (•CH₃) and hydroxyl (•OH) radicals for the oxidation of CH₄ using PdAu nanoparticles.[17] Agarwal et al. used Au-Pd colloids nanoparticles to catalyze CH₄ to CH₃OH with a selectivity of 92%, and the isotopically labeled reactions confirmed that two thirds of H₂O₂ generated •OH to excite •CH₃ generation, and the rest H₂O₂ were decomposed to O₂ into the primary products.[21] The introduction of excessive O₂ could improve the catalytic efficiency by inhibiting the H₂O₂ decomposition and promoting CH₃OH formation. Zhu et al. designed PdAu nanoparticles locked in a zeolite molecular sieve (ZSM-5) with a layer of hydrophobic long-chain alkanes (C₁₆) on the surface.[22] Due to the "molecular fence" effect, in-situ generated H₂O₂ from H₂ and O₂ was enclosed in the ZSM-5-C₁₆, leading to high local concentration of H₂O₂, which significantly improved the utilization of H₂O₂ and the conversion rate of CH₄. These literatures definitely indicated that PdAu nanoparticles could be used as unique and excellent catalysts for CH₄ oxidation. However, the exploration of PdAu catalysts mainly focus on the zero-dimensional (0D) structure with unfavorable structure regulation and size control [21–23] In addition, little has been done on verifying the optimal Au/Pd ration or compositions for maximizing the C1 oxygenated yield and selectivity. Furthermore, few works are reported on revealing the structure-activity relationship and the catalytic mechanisms of CH₄ oxidation is extremely lacking and unclear, not to

^{*} Corresponding authors.

E-mail addresses: dengpeilin@hainanu.edu.cn (P. Deng), tianxl@hainanu.edu.cn (X. Tian).

¹ Y. Xu and D. Wu contributed equally to this work.

mention the precise reaction paths for the oxidation to C1 oxygenated chemicals.[24,25] Generally, one dimensional (1D) NWs displays improved durability and activity owing to the inherent anisotropic, high specific surface area, high conductivity, fast mass transport and excellent flexibility than those of their zero dimensional (0D) counterparts. [26,27] In addition, the 1D structure with extended surface may also provide a desirable model to facilitate modulate the geometric and electronic effects by tuning the compositions.

Inspired by above motivations, herein, we report for the first time that Pd_xAu_y NWs with different Pd/Au atomic ratios are prepared by a facile galvanic replacement reaction, and applied for the efficient CH₄ oxidation under mild conditions. By regulating the Pd/Au ratios and the reaction parameters, including CH₄ concentration, reaction temperature, reaction time, and catalyst amount, the highest C1 productivity of 2890.3 μmol g⁻¹ h⁻¹ with 99% selectivity is realized on Pd₉Au₁ NWs at 70 °C. Comprehensive structural and catalytic characterizations, as well as the density functional theory calculations, demonstrate that the binding affinity between Pd and •CH₃ is so strong that not only restrain the follow-up reactions to C1 liquid, but also resulting in the over oxidation of CH₄ to CO₂. This strong binding affinity can be modulated and weakened by the cooperation of Au, and the follow-up processes is accelerated due to the low reaction barrier of CH₃OH/CH₃OOH formation. In addition, the over oxidation of CH₄ could be limited, endowing a high selectivity to liquid C1 oxygenated products. In a word, the considerable performance and selectivity of Pd₉Au₁ NWs can be attributed to the unique structural and synergistic effects induced by the proper Au decorated Pd sites.

2. Experimental section

2.1. Materials

Sodium tetrachloropalladate (II) (Na₂PdCl₄) and Gold chloride trihydrate (HAuCl₄·3H₂O), Potassium titanium oxalate, 1,2-dichloropropane (99%) was purchased from MACKLIN reagent. Poly(vinylpyrrolidone) (PVP, ~55000), oleylamine (technique grade, 70%, OM) was purchased from Energy Chemical. Potassium iodide (KI) was purchased from Aladdin. Deionized water was used from Smart-mini System (Nison Instrument (Shanghai) Limited) in all our experiments. All chemicals were used as received without further purification.

2.2. Preparation of ultrafine Pd nanowires

Typically, 20 mL PVP aqueous solution (0.04 g/mL) was transferred into a 50 mL Teflon-lined cup under magnetic stirring of 800 rpm. Meanwhile, 6 mL KI aqueous solution (0.1667 g/mL) was added into the Teflon-lined cup with 0.5 mL/min by automatic samplers over 20 min. Subsequently, 10 mL Na₂PdCl₄ aqueous solution (3.6 mg/mL) was added into the Teflon-lined at 0.5 mL/min. After 40 min, the mixture solution was then transferred into a 50 mL stainless autoclave and heated at 200 °C for 2 h. After cooling to room temperature naturally, the solid products were collected by centrifuging at 12,000 rpm for 0.5 h and further purified by deionized water 4 times to get out of excess ions and PVP molecules. Finally, the obtained Pd nanowires (NWs) were re-dispersed into 8 mL deionized water for further using.

2.3. Preparation of Pd_xAu_y bimetallic nanowire

8 mL of 1.25 mg/mL Pd nanowires seeds, 105 mg of PVP, and a certain amount (Table S1) of HAuCl₄ (100 mg/mL) were mixed in a 20 mL glass bottle and held at 60 °C for 3 h under magnetic stirring. After cooling down to room temperature, the solid products were collected by centrifuging at 12,000 rpm for 0.5 h and further purified by a deionized water 5 times to get out of free PVP molecules and ionic species. Finally, the samples were re-dispersed into 10 mL deionized water for further using.

2.4. Preparation of ultrafine Au nanowires

Typically, 4.8 mL of OM and 1.2 mL of 1,2-dichloropropane were vortexed well in 10 mL centrifuge tubes and placed in an ice bath for 2 min, followed by rapid addition to a glass vial containing 3 mg of HAuCl₄·3 H₂O with continued vortex shaking well. The glass vials were sealed and heated in an oil bath at 70 °C for 17 h. The resulting product was collected by centrifugation (3000 rpm, 3 min), washed three times with hexane and then re-dispersed in hexane.

2.5. Characterization of Pd NWs and Pd_xAu_y bimetallic nanowire

Transmission Electron Microscope (TEM) images, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of samples were recorded on a thermoscientific Talos F200X G2 high-resolution transmission electron microscope at 200 kV. X-ray diffraction (XRD) patterns of samples were conducted on a Rigaku Smart-Lab operating at the voltage of 40 kV and the current 40 mA with Cu Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) was conducted on Shimadzu Axis Supra using a Al Kα (hν = 1486.6 eV) radiation source. The Pd/Au atomic ratio was determined by inductively coupled plasma-atom emission spectroscopy (ICP-AES, Agilent 7700). Proton nuclear magnetic resonance (¹H NMR) (CH₃OH, CH₃OOH and HCOOH) were tested by adding 300 μL electrolyte into the 250 μL D₂O (deuterated water) and 25 μL dimethyl sulfoxide solution (6 mM), in which DMSO was used as an internal standard. The one-dimensional ¹H NMR spectrum was measured with water suppression at 4.7 ppm by using a pre-saturation method. The ¹H spectrum peaks of CH₃OH, CH₃OOH and HCOOH are at ~3.3, ~3.6 and ~8.3 ppm, respectively. The ¹H spectrum peak of DMSO is at ~2.6 ppm. Afterward, CH₃OOH was converted to CH₃OH by using hydrazine hydrate (100 μL). The total amount of CH₃OH and CH₃OOH were analyzed by gas chromatograph (GC), and the amount of CH₃OOH was obtained by minusing method. The gas products were tested by GC (Trace 1300 Series, Thermo Fisher) with flame ionization detector (FID). The CO and CO₂ could be converted into CH₄ through the methanator and analyzed by FID. The content of all products was calculated by using the standard curve method. The productivity and the selectivity of all products were calculated by using the following formula (1) and (2).

$$\text{The productivity of products}(\mu\text{mol g}^{-1} \text{ h}^{-1}) = \frac{\text{Products}(\mu\text{mol})}{\text{Catalyst(g)} \times \text{Time(h)}} \quad (1)$$

$$\text{Liquid product selectivity}(\%) = \frac{\text{CH}_3\text{OH} + \text{CH}_3\text{OOH} + \text{HCOOH}(\mu\text{mol})}{\text{All products}(\mu\text{mol})} \times 100\% \quad (2)$$

2.6. Catalytic performance of the direct conversion of CH₄

Methane oxidation was carried out in a 50 mL stainless-steel autoclave containing a quartz liner vessel with 10 mL of colloidal catalyst. The autoclave was sealed and purged three times with feed gas containing 3.3% H₂, 6.6% O₂, 1.6% CH₄, and 61.7% Ar, and 26.8% He and maintaining the pressure at 1.0 MPa. The mixture was stirred at 1200 rpm and heated to specific temperature at the ramp rate of 1.5 °C/min, followed by introducing the feed gas CH₄ and maintaining the pressure at 3.0 MPa, maintained at the reaction temperature for 0.5 h. At the end of reaction, the autoclave was cooled in ice to a temperature below low than 10 °C in order to minimize the loss of volatile products. In order to study the reusability of the catalyst, the colloidal catalyst was separated by centrifugation (12,000 rpm/30 min) after each reaction run. After drying at 80 °C for 12 h in vacuum, the catalyst was reused in the next run.

2.7. The turnover frequency (TOF) of the as-prepared catalysts

$$TOF = \frac{\text{Turnover number for oxygenate formation (TON)}}{\text{Number of active site (N)}}; \text{ units } \text{ish}^{-1}$$

$$TON = n(\text{oxygenate}) \times N_A;$$

n is the amount of substance of the oxygenated products; N_A is 6.02×10^{23} .

$$N = \frac{m \times W}{M} \times N_A$$

N is Number of active sites, m is the amount of substance of Pd, M is the relative atomic mass of Pd, W is the mass fraction of Pd in the catalyst.

2.8. Electron paramagnetic resonance (EPR) test

The detection of free radicals in the reaction process of direct methanol oxidation was performed at a Bruker A320 electron paramagnetic resonance spectroscopy (EPR, Field setting resolution: 1MG (0.1UT)), using 5, 5'-dimethyl-1-pyrroline-N-oxide (DMPO) was used as the scavenger. Typically, 1 mL DMPO-H₂O (100 mmol L⁻¹) was added into 1 mL of reaction mixture. Transfer the mixed solution immediately to the capillary tube (diameter: 0.1 mm; filling liquid height: ~ 5 cm), which was then fixed in the resonant cavity of the spectrometer. Contrast experiments were carried out to determine the type of free radical by the characteristic peaks. Contrast experiment 1 (No. 1) (labeled as DMPO + H₂O₂ + Fe²⁺): 1 mL FeSO₄·7 H₂O (50 mmol L⁻¹) and HNO₃ solution (pH = 4) were mixed with 1 mL DMPO-H₂O (100 mmol·L⁻¹) under vortex oscillation g for 2 min, followed by adding 50 μL of H₂O₂ (30 wt%). No. 2 (labeled as DMPO + H₂O₂ + Fe²⁺ + CH₃OH): all the processes were the same with contrast experiment 1, except for the addition of 1 mL of CH₃OH (100 mmol L⁻¹) into the solution.

2.9. CH₄ temperature-programmed desorption (CH₄-TPD) test

Firstly, 50 mg of the sample was weighed into a reaction tube and dried at 10 °C/min from room temperature to 400 °C. The sample was purged with argon gas (50 mL/min) for 1 h and cooled to 50 °C. In turn, a 5% v/v CH₄/Ar mixture (50 mL/min) is passed through the catalyst base at 50 °C for 0.5 h. And, the Ar gas stream (50 mL /min) was switched for 0.5 h at the same temperature to remove weakly physically adsorbed CH₄ from the surface. Finally, the gas was desorbed under Ar atmosphere at a rate of 5 °C/min to 400 °C and detected by TCD.

2.10. Density functional theory (DFT) calculation

Spin-polarized density functional theory calculations were performed by using the Vienna *Ab Initio* Simulation Package (VASP) [28, 29]. The PBE [30] functional and the projector augmented wave (PAW) [31,32] potential were employed. An energy cutoff of 500 eV and a convergence criterion of 10⁻⁵ eV for self-consistent calculations was adopted. The Pd slab exposed (111) surface with 4 × 4 × 1 supercell and four metal layers were cleaved from the bulk materials and the thickness of the vacuum layer between adjacent slab models was about 15 Å. All structures were fully relaxed until the total force on each atom was less than 0.05 eV/Å. The first Brillouin zone was sampled using a 4 × 4 × 1 Γ -centered k-point mesh. The van der Waals interactions were corrected based on the DFT-D3 scheme [33,34]. COHP [35–37] analysis as implemented in the LOBSTER code³⁸ was carried out with the pbe-VaspFit2015 basis set [38]. The corresponding basis functions of H, C, O, Pd, and Au were 1 s, 2s2p, 2s2p, 4d5s, and 5d6s, respectively. The energy barriers were calculated by using the climbing image nudged elastic

band (CI-NEB) method [39]. The solvent effect was included by using the implicit solvation model as implemented in the VASPsol code [40, 41].

The adsorption energy of the molecule on the surface was defined as $E_{ad} = E_{system} - E_{slab} - E_{molecule}$, where the E_{system} , E_{slab} , and $E_{molecule}$ are the DFT energy of the slab system with molecule adsorbed on the surface, the slab system, and one adsorbed molecule. VASPKIT code [42] and VESTA software [43] were used for calculation pre-processing and post-processing.

3. Results and discussion

3.1. The preparation and characterizations for Pd_xAu_y NWs

Fig. 1a illustrates the synthesis process of Pd_xAu_y NWs by the self-assemble and galvanic replacement method, and the effects of KI and PVP concentrations, reaction temperature and reaction time on the morphology of Pd NWs are systematically investigated (Fig. S1). The average diameter of highly purified Pd NWs is approximately 7.2 nm with some concave and convex sites on the surface of Pd NWs, and the crystal plane spacing of 0.225 and 0.195 nm corresponds well to the (111) and (200) crystal planes of Pd, respectively (Fig. S2). Then a series of high quality Pd_xAu_y NWs with different Pd/Au atomic ratios were rapidly synthesized by tuning the content of Au salt precursors (Figs. S3, S4) [44].

Representative transmission electron microscope (TEM) images show that Pd₉Au₁ NWs exhibits a uniform and serrated morphology with a few microns in length (Fig. 1b). The average diameter of the Pd₉Au₁ NWs at the widest and narrowest positions are 12.9 nm and 6.5 nm, respectively (Fig. S3). The element mapping result shows that Pd elements are mainly distributed in the middle, while Au elements are on the surface of the Pd₉Au₁ NWs, especially the protruding parts of the serrated structure (Fig. 1c). Corresponding EDS elemental analysis result shows that the Pd/Au atomic ratio is close to the value of 9:1 (Fig. 1d). To further track the microstructure of the Pd₉Au₁ NWs, the concave and convex areas are characterized in detail (Fig. 1e-g). As shown in the high-resolution TEM (HRTEM) image of concave part, the interplanar spacing of 2.247 Å is indexed as (111) crystal planes of the inner Pd NWs, while the interplanar spacing of 2.433 Å is attributed to the (111) crystal plane of the outer Au atoms (Fig. 1g). The selected Fourier transform (FTT) results for the inner and outer areas (light blue boxes) show that the crystal orientation of Pd₉Au₁ NWs is consistent with the results of the HRTEM, and there also is a five-fold twinned structure (Fig. 1h, 1i). The atomic diameter of Pd and Au atoms is 0.273 nm and 0.286 nm, respectively, consistent with the theoretical diameters (Fig. 1j). In addition, with increasing of Au content, the structure of Pd_xAu_y NWs gradually changes from a smooth surface to a bead-like structure (Fig. S4). HRTEM images show that Pd NWs are covered by a few Au atoms, and the crystal spacing of Pd atoms gradually decreases due to the compressive strain introduced by the outer Au atoms. Moreover, the corresponding EDS results further demonstrate the precise control for the compositions of Pd_xAu_y NWs by using the galvanic replacement method (Fig. S5). To further confirm the actual chemical compositions of Pd_xAu_y NWs, Pd/Au atomic ratios are obtained from ICP-AES results, which is in agreement with EDS results (Table S2).

X-ray diffraction (XRD) is performed to explored the crystalline structure of Pd_xAu_y NWs (Fig. 2a). Pd NWs is a face-centered cubic structure with the space group *Fm3m*, and the crystal plane of (111) and (200) correspond to the lattice spacing of 0.225 nm and 0.195 nm, respectively, in accordance with the HRTEM results [45]. The crystalline structure of Pd_xAu_y NWs is still similar with the Pd NWs with increasing the Au content because of the low content of Au element. However, the peaks of (111) and (200) crystal planes are shifted towards a higher angle, suggesting the lattice spacing of Pd atoms becomes smaller due to the compression effect resulted from the outer Au atoms, in agreement

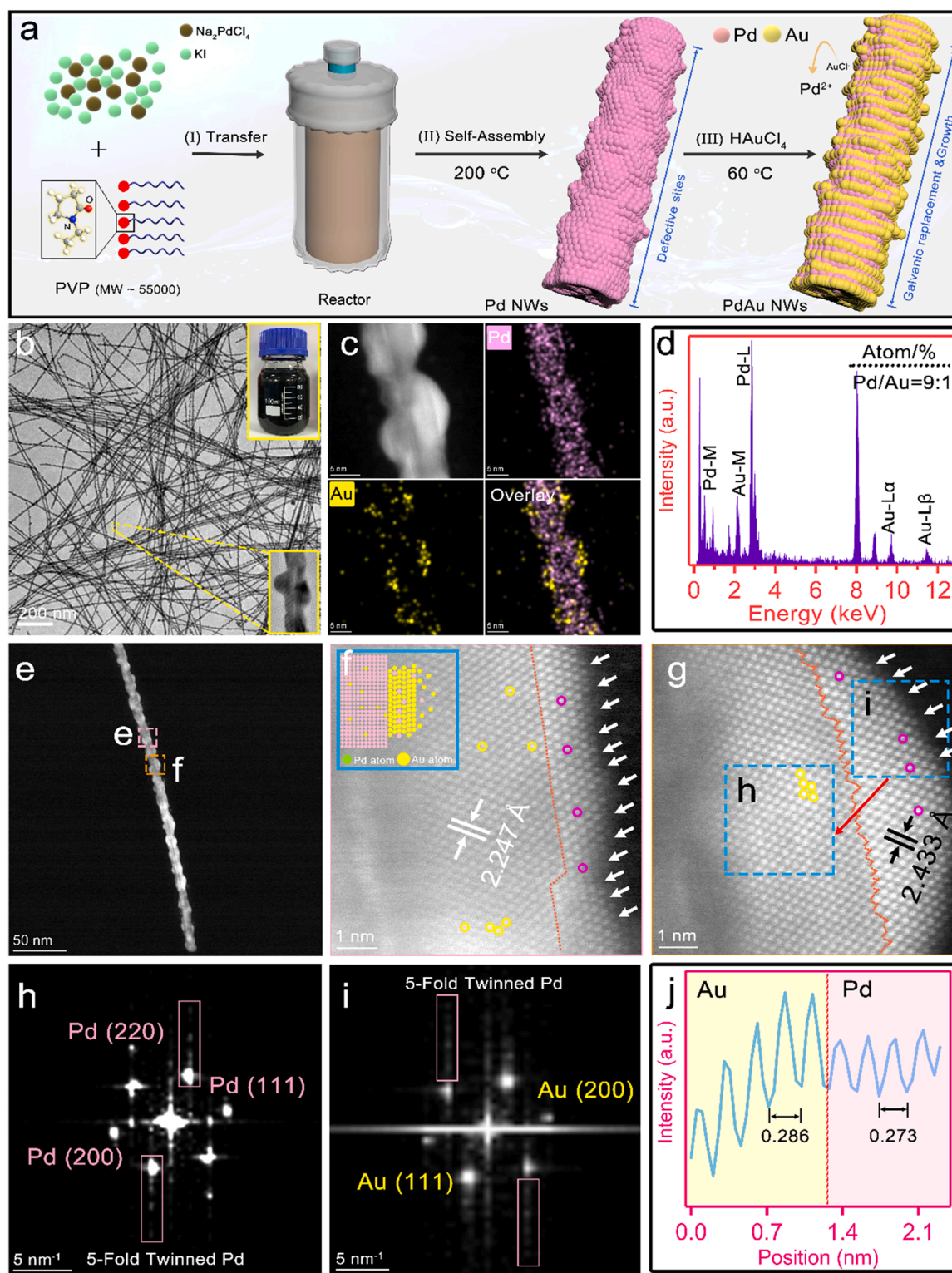


Fig. 1. (a) Schematic illustrations for the synthesis of Pd_xAu_y NWs. (b) TEM image of Pd_9Au_1 NWs (Upper inset: photograph of the as-prepared colloidal solution of Pd_9Au_1 NWs; bottom inset: magnified image of the region in the yellow box). (c) High-angle annular dark-field scanning transmission electron microscopy (HADDF-STEM) images and the corresponding STEM-EDS element mapping of Pd_9Au_1 NWs. (d) TEM-EDS spectrum of Pd_9Au_1 NWs. (e) HADDF-STEM image of a single Pd_9Au_1 NW. (f, g) HRTEM images corresponding to the (e). (h-i) FFT pattern corresponding to (g). (j) Intensity profiles of element along the red lines in (f). (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

with the TEM results (Fig. 2b). X-ray photoelectron spectroscopy (XPS) can reflect the surface chemical state and electronic structure of Pd_xAu_y NWs. As shown in Fig. 2c, the peaks at 335.0 and 340.3 eV are attributed to the $3d_{5/2}$ and $3d_{3/2}$ of metal Pd^0 respectively. Compared with 3d

peaks of Pd NWs, the 3d peaks of Pd_xAu_y NWs exhibit a slight decrease, except for Pd_7Au_1 with higher Au content, which resulted from the litter Au atoms inducing the interaction between Pd and Au atoms. In addition, the oxidized Pd^{2+} species are also detected, corresponding to peaks

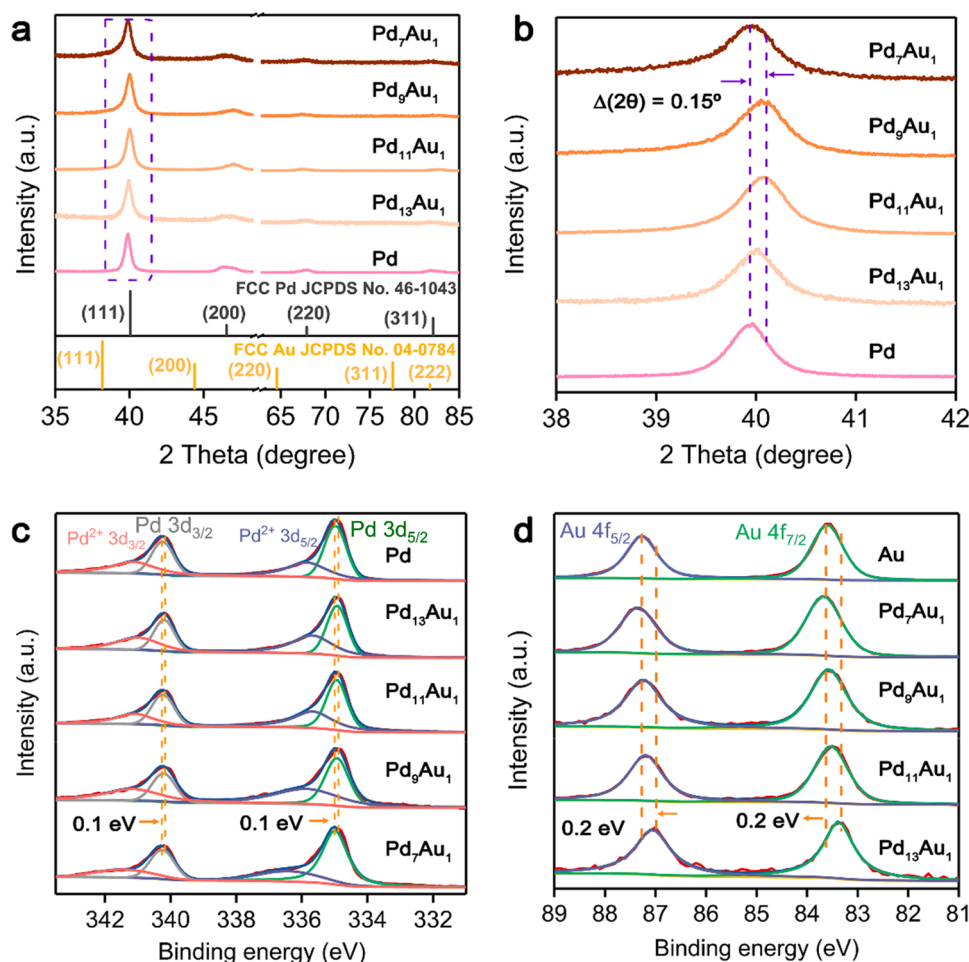


Fig. 2. (a) XRD patterns of Pd and Pd_xAu_y NWs. (b) The magnified image of the region around the crystal face of (111). (c) XPS spectra of Pd 3d for Pd NWs and Pd_xAu_y NWs. (d) XPS spectra of Au 4f for Au and Pd_xAu_y NWs.

of 335.9 eV (3d_{5/2}) and 341.2 eV (3d_{3/2}), respectively, which may be ascribed to the property of easily oxidized Pd atoms in air. As shown in Fig. 2d, the peaks at 83.7 and 87.2 eV are attributed to the 4f_{7/2} and 4f_{5/2} of the metal Au⁰, respectively. The electronic states of 4f peaks shift towards a lower binding energy, indicating the electrons enrichment of Au atoms. The simultaneous negative shift of Pd 3d and Au 4f are attributed that the electrons transfer from inner orbit to outer orbit, demonstrating that the external Au atoms affect the electronic structure of Pd atoms [45]. Moreover, the surface Pd/Au atom ratio in XPS results is obviously higher than the whole Pd/Au atom ratio in the TEM-EDS results because of the Au atom covering the surface of Pd NWs (Table S3).

3.2. The catalytic performance for the direct CH₄ conversion

The catalytic performance of the direct CH₄ oxidations is measured in a sealed pressurized stainless-steel reactor. The gas and liquid products are quantified by gas chromatography (GC) and proton nuclear magnetic resonance (¹H NMR), and the corresponding plots and standard curves of which are shown in Figs. S6–S8. As shown in Fig. 3a, Pd NWs catalyst exhibits a productivity of 1163.1 μmol g⁻¹ h⁻¹ and a selectivity of 96.6% for CH₄ converting to liquid C1 oxygenated products, higher than that of Pd nanoparticles [21,25], which is attributed to the special property of one-dimensional structure. With the decoration of Au atoms, Pd_xAu_y NWs present a higher productivity and selectivity for C1 products (Fig. S9 and Table S4). Obviously, Pd₉Au₁ NWs shows a highest catalytic performance via precisely adjusting the Pd/Au atomic

ratios, corresponding to the productivity of 1738.5 μmol g⁻¹ h⁻¹ and the selectivity of 97.1% at 90 °C, which indicate that Pd₉Au₁ catalysts well activate CH₄ molecule and suppress the over oxidation of CH₄ for direct CH₄ oxidations to liquid C1 products. The comparison results demonstrate that Pd is the active site during direct CH₄ oxidation, and there is not activity for Au atom (Table S5). With the decoration of Au atoms into Pd NWs, Pd_xAu_y NWs show a higher catalytic performance for oxygenated products than that of Pd NWs, indicating the incorporation of Au atoms could affect the intrinsic activity of Pd atoms for direct CH₄ oxidation. To further evaluate intrinsic activity of the Pd NWs and Pd_xAu_y NWs, turnover frequencies (TOFs) are calculated and Pd atoms are served as active sites. Pd₉Au₁ NWs has a highest TOF than Pd NWs and other Pd_xAu_y NWs due to the moderate incorporation of Au atoms into Pd NWs. But more incorporation of Au atoms in turn inhibit intrinsic activity of Pd atoms (Table S6). The effect of various reaction conditions (CH₄ contents, oxidant form, reaction temperature, time and the amount of catalysts) are systematically discussed for the direct conversion of CH₄. Firstly, when the CH₄ content is extremely low, the liquid products are almost not detected (Fig. 3b). However, the appropriate CH₄ content could obtain a highest yield of liquid C1 products, which prove that the liquid C1 products come from the CH₄ conversion (Table S7). Secondly, it is consequently essential to investigate suitable reaction temperature and time to improve the performance of the direct CH₄ conversion. As shown in Fig. 3c, the yield of liquid C1 products behaves an increasing manner from 30 °C to 70 °C with an excellent selectivity. However, the yield and selectivity of liquid products rapidly decrease over 70 °C, and the peroxidation product obviously increased.

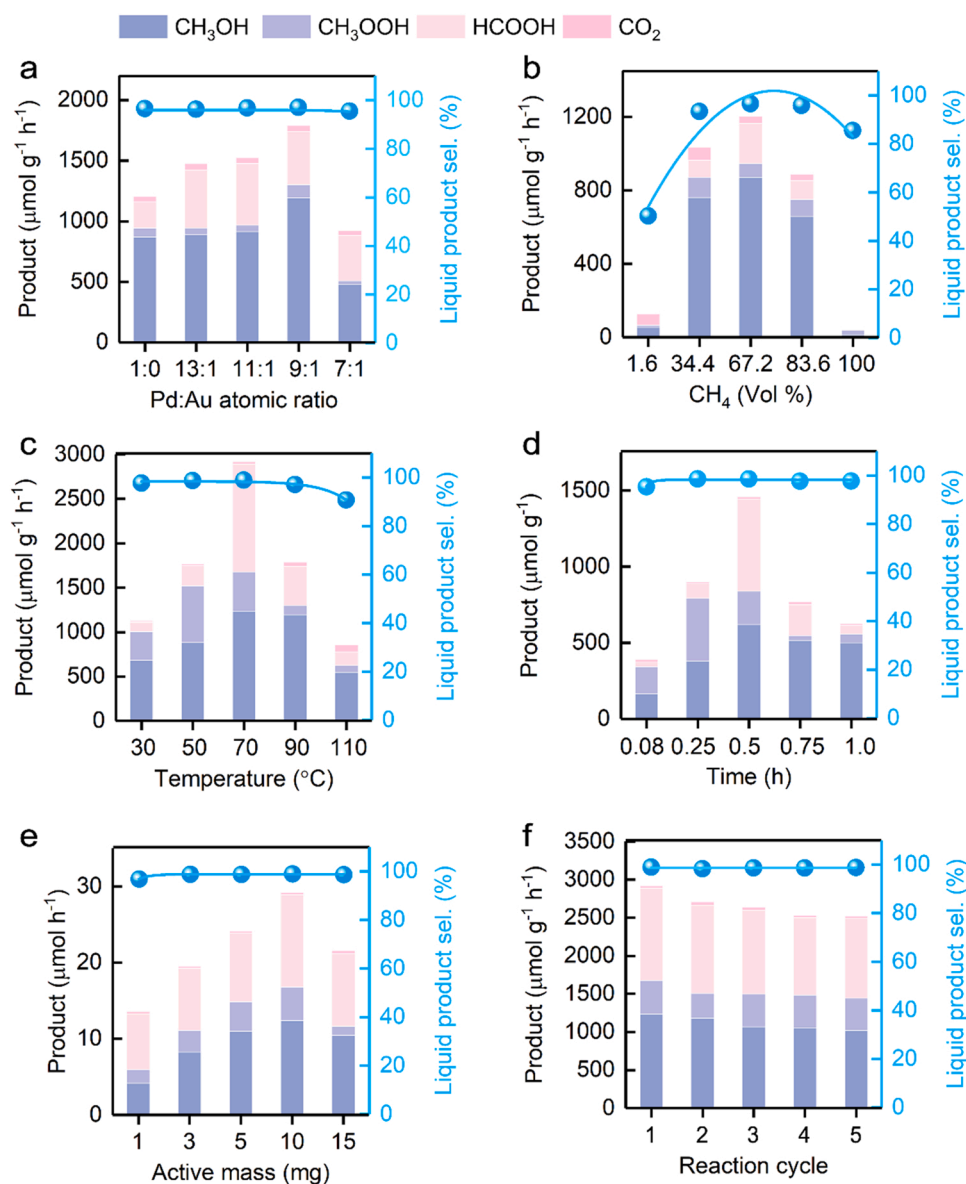


Fig. 3. (a) The yield of products and selectivity of liquid products for Pd and Pd₉Au₁ NWs. Reaction conditions: 0.5 h, 90 °C, 10 mg of catalyst; (b) The catalytic performance with different CH₄ vol. Pd NWs. Reaction conditions: 0.5 h, 90 °C, 10 mg of Pd NWs; (c) The catalytic performance with different reaction temperatures for Pd₉Au₁ NWs. Reaction conditions: 0.5 h, CH₄ of 67.2 vol%, 10 mg of Pd₉Au₁ NWs. (d) The catalytic performance with different reaction time for Pd₉Au₁ NWs. Reaction conditions: 70 °C, 10 mg of Pd₉Au₁ NWs. (e) The catalytic performance with different active mass for Pd₉Au₁ NWs. Reaction conditions: 0.5 h, 70 °C, CH₄ of 67.2 vol%. (f) Reaction tests for the recycle and regeneration of the Pd₉Au₁ NWs catalyst. All other conditions remain the same: 10 mL of water, feed gas at 3.0 MPa with 1.1% H₂/2.2% O₂/67.2% CH₄/20.57% Ar/8.93% He, and 1200 revolutions per minute (rpm).

These results suggest the improved temperature is beneficial for the higher catalytic activity and selectivity for oxygenated products, but the higher temperature could accelerate the generation of by-products, leading to a lower catalytic activity and selectivity for targeted products. The maximum yield of liquid products is 2890.3 μmol g⁻¹ h⁻¹ with a selectivity of 99% at 70 °C for Pd₉Au₁ NWs during direct CH₄ oxidation (Table S8), which is comparable and even much higher than the previously reported literatures (Table S8). When H₂O₂ and H₂O₂/O₂ respectively used as the oxidant, the productivity of liquid C1 products for Pd₉Au₁ NWs only reaches 324.7 μmol g⁻¹ h⁻¹ and 129.0 μmol g⁻¹ h⁻¹ (Table S10). These results are dramatic lower than the value (2890.3 μmol g⁻¹ h⁻¹) with in situ formation of H₂O₂ from O₂ and H₂, which demonstrate that the in-situ H₂O₂ generation favors to accelerate CH₄ oxidation [17,22]. In addition, the yield of liquid C1 products gradually increases with the extension of reaction time, and the reaction time of 0.5 h reaches the highest yield of liquid products (Fig. 3d), while prolonged reaction time leads to the deep oxidation of liquid products to CO₂ (Table S11). Furthermore, the yield of liquid C1 products increases with increasing the amount of Pd₉Au₁ NWs (Fig. 3e), while the yield fleetly decreases with excessive catalysts, which may be explained by the restricted mass transfer (Table S12). Moreover, Pd₉Au₁ NWs exhibits

excellent catalytic performance during five cycles, maintaining more than 90% of the initial yield of liquid C1 product as well as negligible variation in selectivity (Fig. 3f). More importantly, there is essentially no change in the morphology can be observed, demonstrating the high cycling and structural stability of Pd₉Au₁ NWs (Fig. S11).

3.3. Mechanism insights into CH₄ activation and C1 products generation

To clarify the reaction mechanisms of Pd_xAu_y NWs for the direct conversion of CH₄, the key reaction steps are analyzed, especially CH₄ decomposition step and H₂O₂ formation step. As illustrated in Fig. 4a, the typical ¹H NMR spectrum peaks of CH₃OH, CH₃OOH and HCOOH are at ~3.3, ~3.6 and ~8.3 ppm, respectively. First of all, the CH₃OOH is mainly formed during the direct CH₄ oxidation at 0.08 h. With time up to 0.5 h, CH₃OOH showed a decreasing trend, while CH₃OH and HCOOH showed an increasing tendency, which heralded a conversion of CH₃OOH to CH₃OH and HCOOH. Meanwhile, the in-situ generation of H₂O₂ from O₂ and H₂ can be occurred with the catalysis of PdAu NWs, which is confirmed by the titanium oxalate spectrophotometric method (Fig. S12 and Table S13) [21,22,46]. The generation of H₂O₂ is along with the direct CH₄ oxidation, which demonstrate that the trigger of CH₄

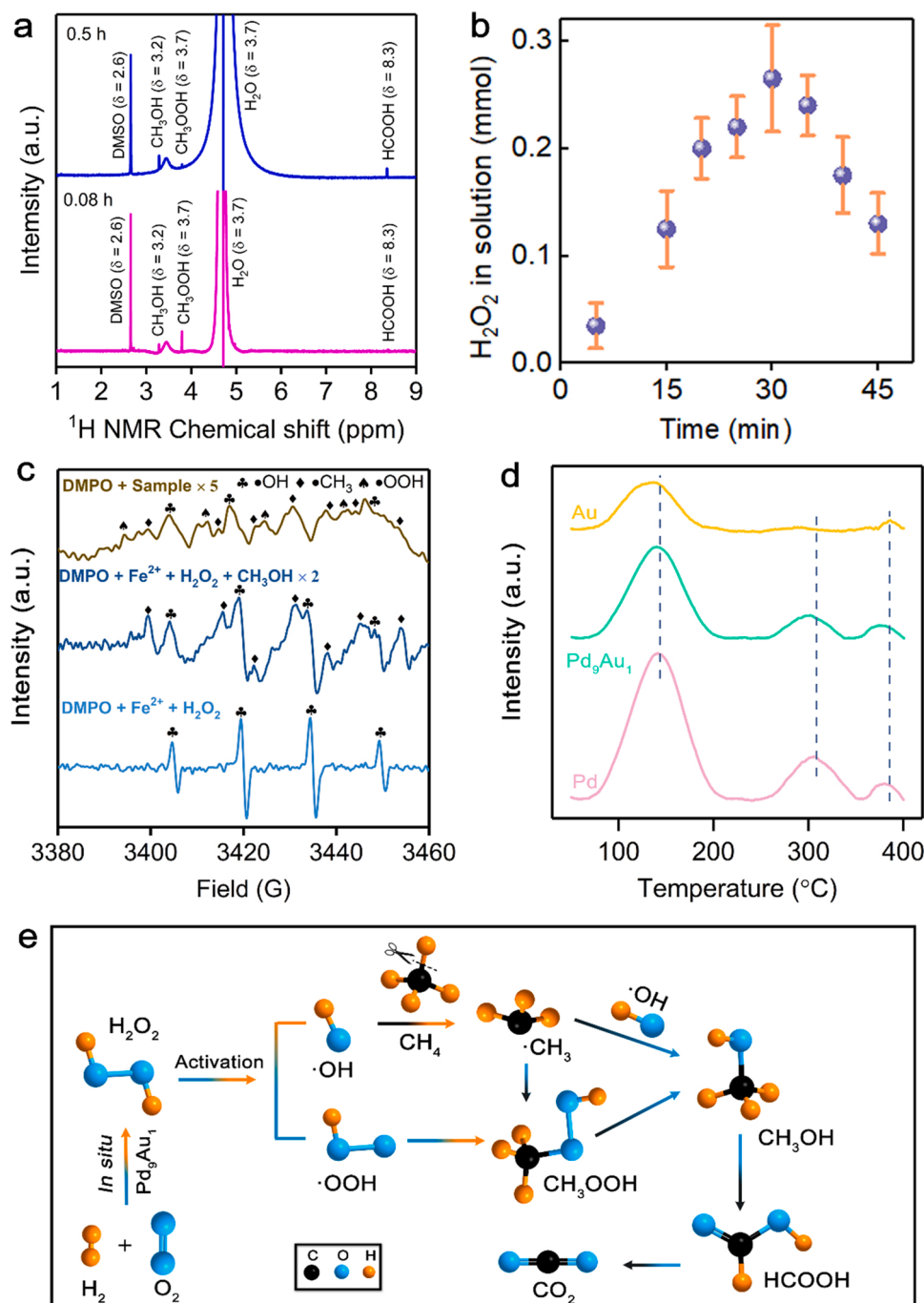


Fig. 4. (a) ^1H NMR spectra of liquid products with the reaction time of 0.08 h and 0.5 h, respectively; (b) The time-dependency of in situ generation H_2O_2 productivity for 90 $^\circ\text{C}$ in O_2 and H_2 atmosphere. (c) The signal of EPR spectrum of radical species ($\bullet\text{CH}_3$, $\bullet\text{OH}$, $\bullet\text{OOH}$); (d) CH_4 -TPD of Pd NWs, Au NWs and Pd_9Au_1 NWs, respectively; (e) The proposed reaction mechanism of the direct CH_4 oxidation to liquid products.

decomposition step requires the presence of $\bullet\text{OH}$ radical from H_2O_2 (Fig. 4b). Meanwhile, the content of H_2O_2 is gradually increasing with reaction time prolonging. The highest content of H_2O_2 corresponds to the optimal reaction time during the direct CH_4 oxidation. As shown in Fig. 4c (from top to bottom), DMPO (5, 5'-dimethyl-1-pyrroline-N-oxide) is used as the scavenger and additionally ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$) and ($\text{H}_2\text{O}_2 + \text{Fe}^{2+} + \text{CH}_3\text{OH}$) are added as contrast experiments, respectively, which show the presence of $\bullet\text{OH}$, $\bullet\text{OOH}$ and $\bullet\text{CH}_3$ radicals in the reaction systems, further confirming that the direct CH_4 oxidation is triggered by the free radical process of $\bullet\text{OH}$. [17] In addition, the temperature programmed desorption (TPD) not only reflects the binding capacity between the adsorbent and the catalysts surface, but also the

kinetic behavior at the temperature and surface coverage during desorption occurs. As depicted in Fig. 4d, the Au NWs, having a similar structure with Pd NWs (Fig. S13), shows a desorption peak at 130 $^\circ\text{C}$, while Pd NWs has three desorption peaks at 140 $^\circ\text{C}$, 310 $^\circ\text{C}$ and 390 $^\circ\text{C}$, respectively. These results indicate that there is a weak CH_4 adsorption capacity for Au NWs to go against the CH_4 activation, which prove the sluggishness of Au NWs for CH_4 direct oxidation as prove by the experiment (Table S4). However, Pd atoms exhibit a strong CH_4 adsorption capacity, while the strong interaction may lead to the difficulty in the subsequent processes for the CH_4 oxidation. With the addition of Au, the desorption peaks move towards the lower temperature and a much higher performance for CH_4 oxidation is obtained,

which proves that the moderate adsorption capacity is beneficial for the CH_4 activation and the following generation of liquid C1 products. Therefore, based on above results, the reaction mechanisms for the conversion of CH_4 to liquid C1 products are proposed with three steps (Fig. 4e): (1) Firstly, the H_2O_2 is in situ generation from O_2 and H_2 by catalyzed PdAu NWs, then which could form $\bullet\text{OH}$ and $\bullet\text{OOH}$ radicals; (2) Simultaneously, CH_4 adsorbed on PdAu NWs surface is activated with $\bullet\text{OH}$ to form $\bullet\text{CH}_3$ radical by controllable breaking the C-H bond; (3) The combination of $\bullet\text{CH}_3$ radical with $\bullet\text{OH}$ or $\bullet\text{OOH}$ radicals to form CH_3OH or CH_3OOH , respectively. Then CH_3OOH fast converts to CH_3OH , which could be over-oxidated to a spot of HCOOH and CO_2 products via a multi-step radical activation process.

3.4. Effect of Au atoms decorated Pd NWs for CH_4 conversion

The density function theory (DFT) calculations are carried out to further illuminate theoretical insights into the mechanisms of CH_4 oxidation on PdAu NWs. Two slab models, Pd slab and PdAu slab, are displayed in Fig. 5a and Fig. 5b, respectively. As summarized in Table S14, the adsorption of CH_3^* , OH^* , and OOH^* on Pd surface is

strong with a large adsorption energy (E_{ad}) of -2.11 , -2.70 , and -1.31 eV, respectively, while it's relatively weak with a smaller E_{ad} of -1.88 , -2.21 , and -0.92 eV on the PdAu surface. The corresponding adsorption configurations of Pd and PdAu slab are displayed in Fig. 5c and Fig. 5d, respectively. The integrated crystal orbital Hamilton population (ICOHP) at the Fermi level between the adsorbent and the slab, which has got great success to correlate the adsorption strength with the electronic structure [47–50], is calculated. A more negative ICOHP indicates the stronger chemical bond between the adsorbed radicals and the surface. As shown in Fig. 5e and Table S15, the ICOHP for CH_3^* , OH^* , and OOH^* on Pd surface is -2.44 , -3.31 , and -3.34 , respectively, while it's -2.31 , -2.04 , and -2.08 on PdAu surface. These results demonstrate that the existence of Au enables to modulate the interactions between the intermediates and Pd atoms (Fig. S14 and Table S15), leading to a weaker adsorption strength for the intermediates on the PdAu surface, which offers opportunity to optimize the CH_4 conversion performance.

Both of the CH_3OH and CH_3OOH paths are investigated on the Pd and PdAu surface, and each path can be divided into two stages (Figs. 5f and 5g), that is, the CH_4 activation stage (stage-I) and CH_3OH (or

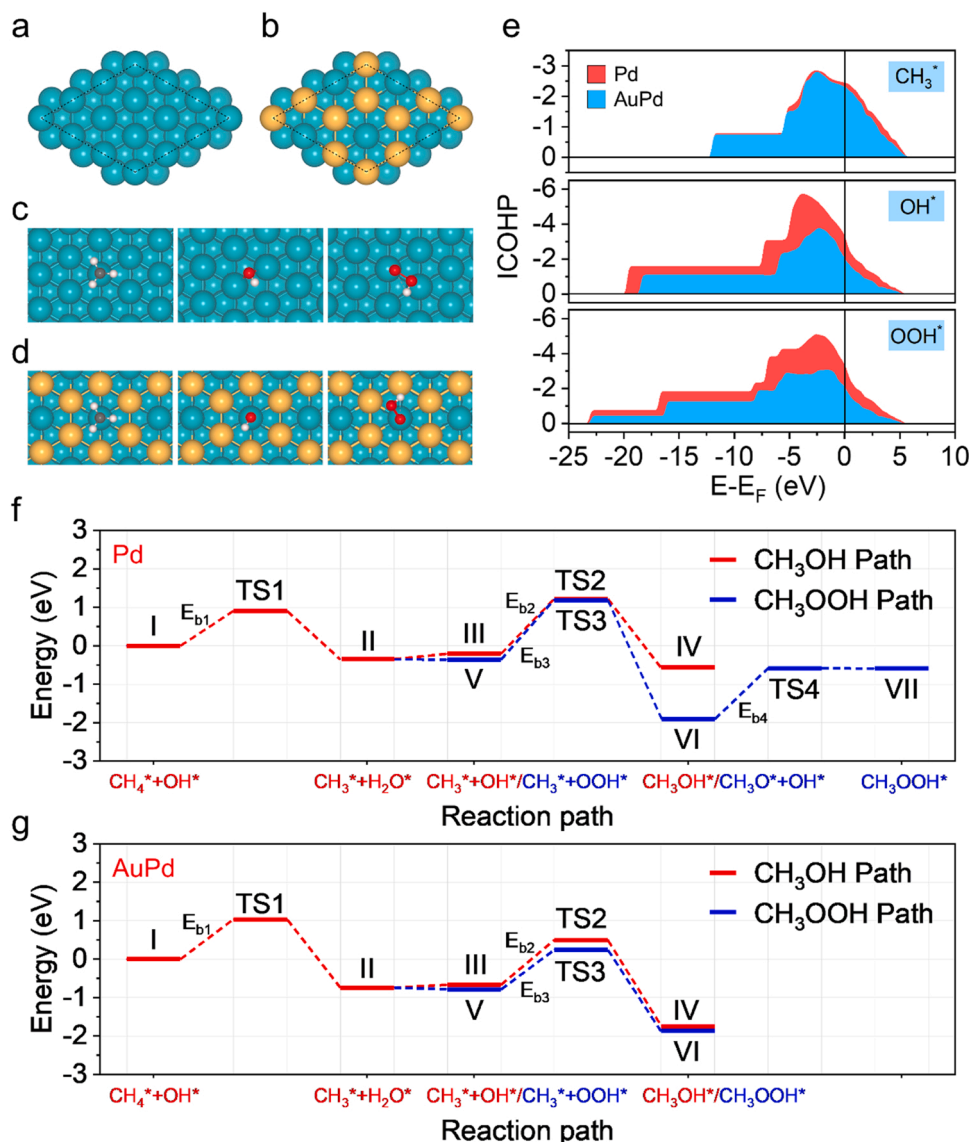


Fig. 5. Crystal structure of (a) Pd slab and (b) PdAu slab. Adsorption configuration of CH_3^* , OH^* , and OOH^* on (c) Pd slab and (d) PdAu slab. (e) ICOHP results. Reaction path on the (f) Pd surface and (g) surface. The balls in cyan, gold, red, grey, and white represent Pd, Au, O, C, and H atoms, respectively. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

CH₃OOH) formation stage (stage-II). The CH₃OOH produced in the CH₃OOH path would be further oxidized to CH₃OH. All the relevant structures are summarized (Figs. S15, S16). The energy barrier (E_b), defined as the energy difference between the initial state and the highest transition state, in each elementary reaction are evaluated to access the CH₄ oxidation performance of the catalyst. For the Pd slab, the E_b is estimated to be 1.21 eV (I → TS2) and 1.19 eV (I → TS3) for CH₃OH and CH₃OOH path, respectively (Fig. 5f). At stage-I, CH₃* groups are produced by the reaction of CH₄ and OH* with an E_b of 0.90 eV (I → II). Afterwards, the reaction of stage-II for CH₃OH path (III → IV) exhibits a high E_b of 1.42 eV due to the strong adsorption of CH₃* on the Pd surface. Note that in the stage-II for the CH₃OOH path, there are two transition states, the decomposition of OOH* to produce CH₃O* and OH* (V → VI, E_{b3} = 1.55 eV) and the thermodynamically unfavorable CH₃OOH* formation (VI → VII, E_{b4} = 1.32 eV), which suggests that the CH₃OOH path is limited on the Pd surface. As illustrated in Fig. 5g, the elementary reactions are all exothermic on the PdAu surface, and the E_b of stage-II for CH₃OH and CH₃OOH path is 1.17 (III → TS2) and 1.03 eV (V → TS3), respectively, much smaller than those (1.32 ~ 1.55 eV) on the pure Pd surface owing to the weaker adsorption of CH₃* on PdAu surface, implying that both of CH₃OH and CH₃OOH formation on PdAu surface are accelerated. Moreover, the apparent E_b is 1.03 eV (I → TS1) on the AuPd surface, also smaller than those on the pure Pd surface (1.19 ~ 1.21 eV). The DFT results demonstrate that alloying with Au enables to modulate the adsorption strength between the intermediate radicals and Pd atom, and the reaction pathways can also be optimized, promoting the direct conversion of CH₄ to C1 products.

4. Conclusions

In summary, Pd_xAu_y NWs with high quality are systematically investigated for the structure-activity relationship between PdAu and the CH₄ oxidation performance. The experimental results indicate that the unique 1D structure, the compositions of PdAu NWs and the reaction conditions affect the performance of the direct CH₄ oxidation to liquid C1 products. Pd₃Au₁ NWs show a maximum yield of 2890.3 μmol g⁻¹ h⁻¹ and a 99% selectivity for liquid C1 products at 70 °C. More importantly, the probably reaction pathways for the direct CH₄ oxidation to C1 products are proposed, and DFT results clearly reveal that the moderated binding strength between the intermediates (OH*, OOH*, CH₃*) and Pd atoms by the incorporation of Au facilitates the C-H activation and targeted products generation. This study provides deep insights to improve the performance of PdAu catalysts in the direct CH₄ conversion to high added-value chemical feedstocks.

CRediT authorship contribution statement

Yueshan Xu: Conceptualization, Investigation, Visualization, Writing – original draft. **Daoxiong Wu:** Investigation, Resources, Visualization, Writing – original draft. **Peilin Deng:** Conceptualization, Investigation, Writing – original draft, Resources. **Jing Li:** Investigation, Resources. **Junming Luo:** Investigation, Resources. **Qi Chen:** Investigation. **Wei Huang:** Investigation. **Chong Michael Shim:** Investigation. **Chunman Jia:** Investigation. **Zhongxin Liu:** Investigation. **Yijun Shen:** Investigation. **Xinlong Tian:** Conceptualization, Project administration, Supervision, Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2022.121223.

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